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# Pentane transformations over sulfated alumina catalyst

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**Abstract** The transformation of n-pentane at 295 K in the presence of catalysts of defined acid strength from $-9.6$ to $-15$ $H_O$ units were studied. The results were compared with those for $Al_2O_3-SO_4^{2-}$ (8 %) of acid strength equal to $-11.5 < H_O \leq -10.8$. It was found that: (a) for superacids of acid strength $H_O < -13$, the reaction begins with the protonation of the C–H $\sigma$ bond of a pentane and proceeds according to the bimolecular mechanism; (b) for less acidic catalysts such as sulfated alumina, pentane is oxidized to pentene, which is converted to the pentyl cation after protonation. The latter reacts in the presence of catalysts of acid strength of at least $H_O$ equal to $-9.6$ according to two pathways: (a) unimolecular at an excess of $H^-$ (in the presence of additional hydride donor pentane co-substrate) with selective formation of 2-methylbutane; (b) bimolecular in the absence of $H^-$ (pentane alone is the substrate). In the latter case, the transformation proceeds through the formation of a ten-carbon dimer cation state, which upon decomposition leads to 2-methylpropane, 2-methylbutane and unsaturated coke precursors.

**Keywords** Pentane · Isomerization · Superacids · Sulfated alumina

## Introduction

Sulfated oxides have been among the most studied solid acids for decades. This has been due to their high acid strength, which makes them capable of catalyzing the isomerization of light alkanes (butane–hexane) even at ambient temperature [1]. A vast amount of published results concerning superacids has led to the conclusion

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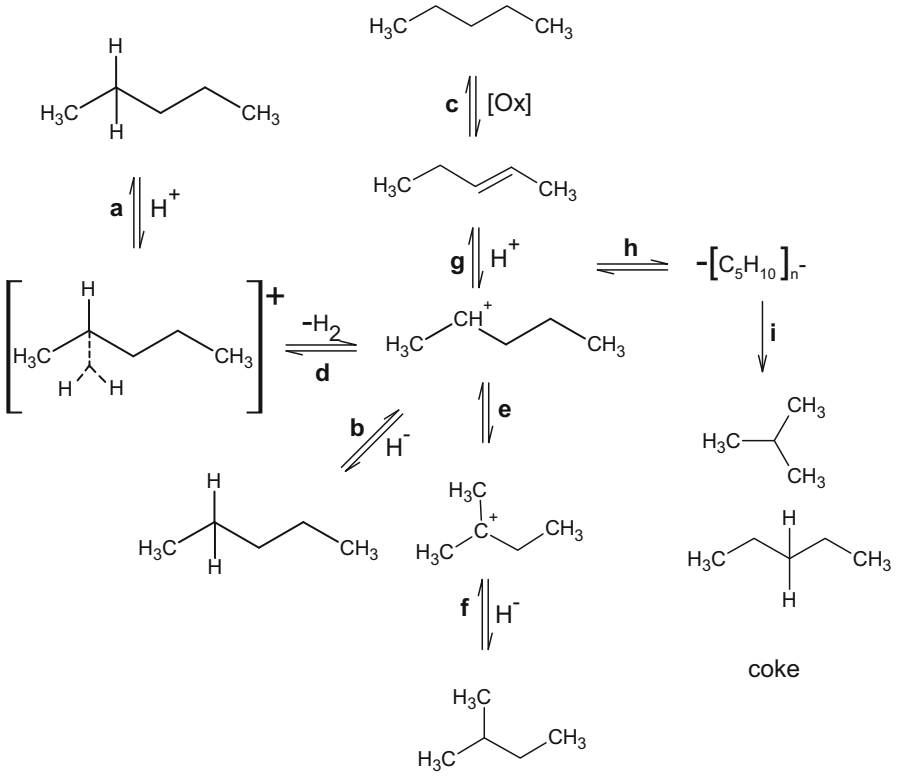
that alkanes undergo transformation according to two main mechanisms. The first mechanism, characteristic of superacids of high acid strength, describes the reaction of pentane with a proton to form a carbonium ion, which decomposes to hydrogen and a carbenium ion [2, 3] (Scheme 1).

The pentyl cation isomerizes to a tertiary carbenium ion and after reacting with a hydride ion, 2-methylbutane, the main product is obtained. The second mechanism describes the reaction of pentane with superacids of acid strength closer to the lower limit of the superacid region. In the presence of such catalysts, pentyl cation undergoes deprotonation to pentene, which would react with another pentyl cation to form a dimeric cation. After isomerization and subsequent β-scission, the dimeric cation produces both 2-methylpropane and 2-methylbutane [4, 5]. The remaining unsaturated decomposition reaction products became coke precursors. The catalysts that are not acidic enough to convert pentane via the carbonium to carbenium ion pathway but possess active redox sites catalyze the oxidation of pentane to pentene as the initial step. The latter compound, being more basic than pentane, could undergo protonation by weaker than superacid Brønsted acid sites to form pentyl cation, which can participate in all the transformation described above.

Sulfated zirconia can be said to be the most studied sulfated oxide. It is postulated that pentane (or butane) isomerization can proceed according to two




**Scheme 1** Pentane transformation over acid and acid-redox catalysts

mechanisms: a unimolecular (involving superacid centers) [6], and a bimolecular (involving the activity of redox and acidic sites) [7, 8] or both mechanisms simultaneously [9]. Much less work has been presented regarding other sulfated oxides such as the $Al_2O_3/SO_4^{2-}$ system, which has been found to possess Brønsted acid centers of acid strength: −5.6/−3, −10.8, −13.8 or even −14.6 $H_O$ units [9–11]. It can therefore be classified as a superacid or at least a strong acidic catalyst. On the other hand, it has been also postulated that sulfate surface groups possess redox properties [12–14]. This means that pentane transformation over sulfated alumina could occur according to all the pathways described in Scheme 1. Moreover it has also been postulated that Lewis acid centers could initiate pentane transformation [5, 15, 16]. Hence, irrespective of which active sites initiate the reaction, pentyl cations formed should react in the same way. It is then obvious that the pentyl cation/pentene transformation should be the most important part of pentane reaction mechanism. Kazansky [17] described pentene reactions that take place in the presence of sulfuric acid–$H_2O$ solutions of different acid strength. For solutions containing from 65 to 80 wt% of $H_2SO_4$ ($-7.5 < H_O \leq -5.1$), 1-pentene undergoes oligomerization (mostly di- and trimerization) forming isomeric decenes and pentadecenes. When sulfuric acid concentration is raised to 95 % ($H_O = -9.8$), $C_{8-13}$ alkanes originating from the consecutive decomposition of oligomers as well as cyclopentene derivatives, appear among the reaction products. Since this work focused on the liquid products of pentene transformation, there is no information on 2-methylbutane or 2-methylpropane formation. However, these products would most probably be obtained, especially for the acid solutions with the highest concentration.

The study of the reactions of pentane as well as the compounds which are considered as precursors of the transition states described in Scheme 1 in the presence of the catalysts of broad acid strength limits i.e. from −9.6 to −15 $H_O$ units are presented. The following compounds were selected as reactants: 1-pentene (reaction intermediate and pentyl cation precursor), 2-bromopentane, 2-bromo-2-methylbutane (pentyl cations precursors), decane, 1-decene, 2-methylnonane, 1-bromodecane, 1-bromo-3,7-dimethyloctane, a mixture of α-olefins ($C_{12-22}$), octane and isooctane (long chain carbocations precursors). The results are expected to clarify the low temperature pentane reaction scheme and to draw conclusions on the acid strength of the $Al_2O_3/SO_4^{2-}$ catalytic system.

## Experimental

γ-$Al_2O_3$ (ABCR, $S_{BET} = 205\ m^2\ g^{-1}$), $SiO_2$ (ABCR Karlsruhe, $S_{BET} = 266\ m^2\ g^{-1}$) as well as sulfated alumina containing 8 % $H_2SO_4$ [18] were used as carriers or catalysts. The catalysts of defined acid strength were obtained according to the following procedure: $SiO_2$ (0.125 g) was impregnated with an acid solution of known acid strength $H_O$ (0.25 $cm^3$). The use of $H_2SO_4$–$H_2O$ solutions allowed for the synthesis of catalysts of acid strength from −5 to −11 $H_O$ units [19], $F_3CCOOH$–$F_3CSO_3H$

system and $FSO_3H$ were used to the range of acid strength to $H_O = -15.1$ [20, 21]. The liquid film of acids filling the pores of the inert silica was a proper catalyst.

Specific surface areas ($S_{BET}$) and pore size distributions (PSD) were measured using an ASAP 202 (Micromeritcs Instrument Co) instrument. BET and BJH isotherms (nitrogen adsorption at 77 K) were applied to calculate $S_{BET}$ and PSD, respectively.

In catalytic reactions, 0.5 g of $Al_2O_3-SO_4^{2-}$ (8 %) was placed in a batch reactor (75 $cm^3$) and calcined at 753 K in dry air. After 3 h, the reactor was closed and cooled to reaction temperature i.e. 295 K, and then the chosen reactants were injected (0.2 $cm^3$). The gaseous products were analyzed after 20 h of reaction. Reactions with the catalysts of known acid strength were performed with the same procedure. 0.125 g of $SiO_2$ was placed in a batch reactor (75 $cm^3$) and impregnated according to incipient wetness method with 0.25 $cm^3$ of acid solution of known acid strength and then particular reactants were injected (0.2 $cm^3$). The reactants vaporized immediately upon injection. The gaseous reaction products were analyzed after 24 h of reaction at 295 K.

The reaction substrates, 1-pentene, 2-bromopentane, 2-bromo-2-methylbutane, decane, 1-decene, 1-bromo-decane, 1-bromo-3,7-dimethyloctane, a mixture of α-olefins ($C_{12-22}$), octane and isooctane were used as cyclohexane mixtures (1:1 molar ratio). In the case of the substrate-cyclohexane (1:1)/methylcyclopentane, the ratio was equal to 1:2. The reaction of 1-pentene with 2-bromopenate was performed using a solution containing the substrates and cyclohexane in equimolar proportions.

The products of all reactions were analyzed by a GC (Agilent 6890 N with FID detector) equipped with a 100 m HP1 capillary column (I.D. 0.25 mm, $d_f$ 0.5 μm, temperature 323 K). Cyclohexane present in the substrates was utilized as an internal standard which in calculation of the conversion to surface oligomers, which were not contained in the reaction products.

All organic reactants were supplied by Aldrich. Only α-olefins $C_{12-22}$ were produced by Shell.

## Results

The specific surface area ($S_{BET}$) for the alumina support for $\gamma$-$Al_2O_3-SO_4^{2-}$ (8 %) was 205 $m^2\ g^{-1}$ and its pore size distribution is presented in Fig. 1.

The most abundant pore diameter was in the 2.3–9.5 nm range. The $S_{BET}$ value of the support remained practically unchanged after the introduction of $H_2SO_4$ (8 wt%) and calcination at 753 K. However, pores of higher diameters (up to 20 nm) were observed. The $S_{BET}$ and pore size distribution of the inert support ($SiO_2$) for liquid acid phases were also determined and found to be 266 $m^2\ g^{-1}$ and pore diameters of between 6 and 15 nm (Fig. 2).

### The influence of catalyst acid strength on n-pentane transformation

The results of n-pentane, decane, 1-decene and 2-methylnonane reactions performed at 295 K depended on the acid strength of the catalyst (Fig. 3).

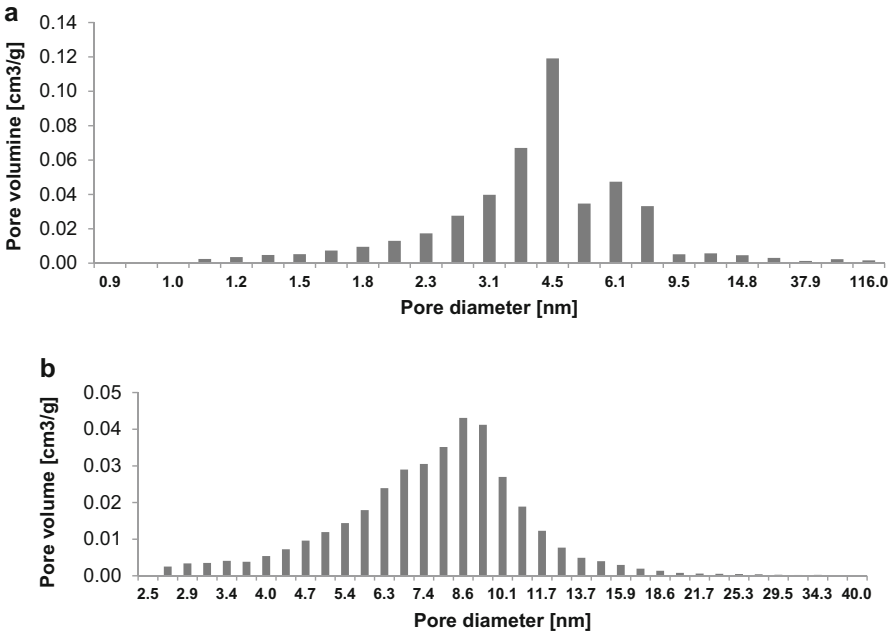



**Fig. 1** Pore size distribution for: **a** $\gamma$-$Al_2O_3$ and **b** $\gamma$-$Al_2O_3-SO_4^{2-}$ (8 %)

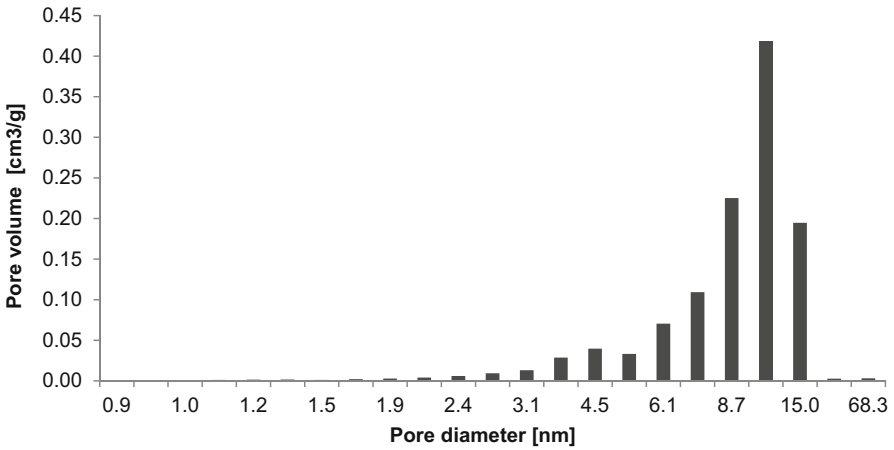



**Fig. 2** Pore size distribution for $SiO_2$

Different acids and acid solutions of known acid strength, dispersed in the pore structure of silica were used as catalysts. Pentane began to react when the acid strength of a catalyst ($H_O$) exceeded the value of $-13$ units. The other reactants which can participate in the pentane reaction, i.e. 1-decene, 2-methylnonane,

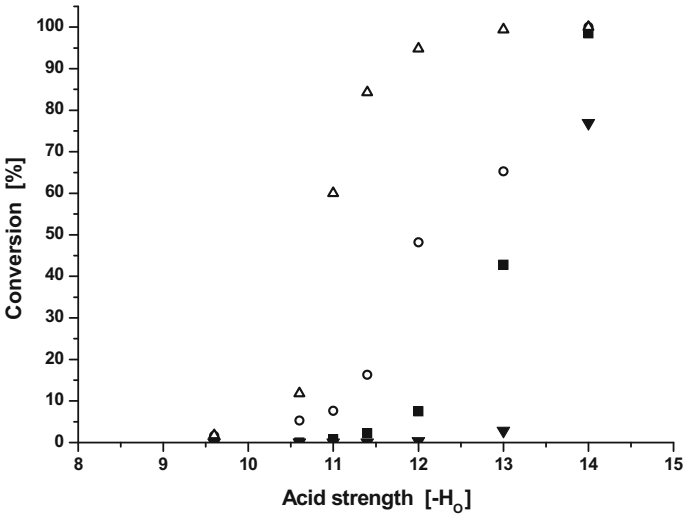



**Fig. 3** Dependence of: decane (*filled square*), 2-methylnonane (*open triangle*), 1-decene (*open circle*), pentane (*inverted filled triangle*) conversion on the catalyst acid strength [catalyst: $SiO_2$–$H_2SO_4$–$H_2O$, $SiO_2$–$F_3CCOOH$–$F_3CSO_3H$ or $SiO_2$–$FSO_3H$ 0.1263 g, temperature 295 K, reaction time 20 h, batch reactor (74 $cm^3$), substrate: 0.2 $cm^3$(1:1 mixture with cyclohexane)]

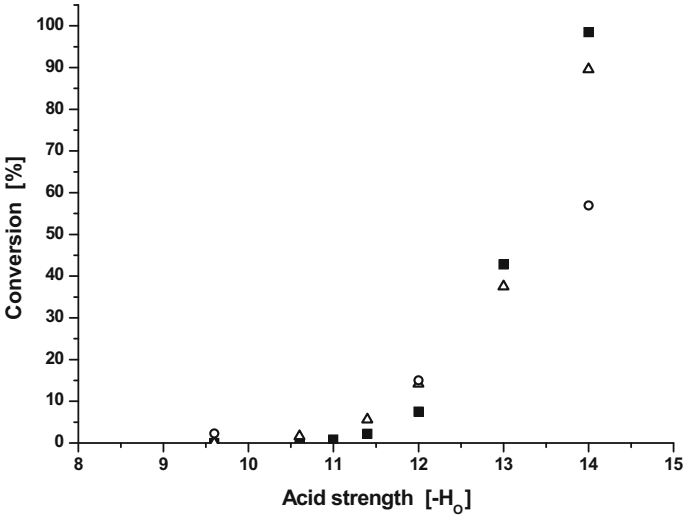



**Fig. 4** Dependence of: decane (*filled square*), 1-bromo-3,3-dimethyl-octane (*open triangle*), 1-pentene (*open circle*) conversion [catalyst: $SiO_2$–$H_2SO_4$–$H_2O$, $SiO_2$–$F_3CCOOH$–$F_3CSO_3H$ or $SiO_2$–$FSO_3H$ 0.1263 g, temperature 295 K, reaction time 20 h, batch reactor (74 $cm^3$), substrate: 0.2 $cm^3$(1:1 mixture with cyclohexane)]

undergo transformation from $H_O \leq -9.5$ while for decane, an acid strength of $H_O \leq -11.5$ was required for reactions to take place. 2-Methylpropane and 2-methylbutane were identified as gaseous products in all the reactions.

The reactions of 1-pentene and 1-bromo-3,7-dimethyl-octane, precursors of carbenium ions, which take part in pentane transformations were also studied (Fig. 4).

In the presence of acids, 1-pentene undergoes protonation while alkyl bromides formed carbenium ions, which were active in the alkylation reactions [22]. The reactions of 1-pentene and 1-bromo-3,7-dimethyl-octane were initiated when the acid strength of a catalyst attained the $H_O \leq -9.6$ level.

In order to examine the possible reactions of intermediates and transition states (carbenium ions formed in situ) in pentane transformation, the reactions of some chosen substrates were studied over a catalyst of $H_O = -9.6$ at 295 K. The reactions were performed for two types of substrates: pure compounds forming 1:1 solutions in cyclohexane and their mixtures (1:2) with a hydride ion donor i.e. methylcyclopentane (Table 1).

Secondary carbenium ion precursors 1-pentene and 2-bromo-pentane, as well as the tertiary carbenium ion precursor 2-bromo-2-methylbutane reacted to obtain 2-methylpropane and 2-methylbutane. The presence of methylcyclopentane in the reaction system led to an increase in the substrate conversion as well as a rise in the 2-methylbutane to 2-methylpropane ratio. 1-Decene and α-olefins $C_{12-24}$ decomposed to 2-methylpropane and 2-methybutane, but these reactions were inhibited by the presence of a hydride anion donor.

**Table 1** Pentane reaction. The transformation of carbenium ions precursors

| Substrate | $H^-$ donor | Conversion (%) | Selectivity (%) | |
|---|---|---|---|---|
| | | | 2-MPr | 2-MB |
| 1-Pentene | – | 9.0 | 64.4 | 35.6 |
| 1-Pentene | MCP | 31.0 | 34.5 | 65.5 |
| 2-Bromopentane | – | 1.7 | 47.1 | 52.9 |
| 2-Bromopentane | MCP | 9.8 | 11.2 | 88.8 |
| 2-Bromo-2-methylbutane[a] | | 16.9 | 37.3 | 62.7 |
| 2-Bromo-2-methylbutane[a] | MCP | 74.3 | 28.5 | 71.5 |
| 1-Pentene + 2-bromopentane | – | 16.1 | 52.2 | 47.8 |
| 1-Pentene + 2-bromopentane | MCP | 39.3 | 21.1 | 78.9 |
| 1-Decene | – | 1.2 | 93.3 | 6.7 |
| 1-Decene | MCP | 0.0 | 0.0 | 0.0 |
| Alkenes $C_{12-24}$ | – | 1.6 | 75.0 | 25.0 |
| Alkenes $C_{12-24}$ | MCP | 0.0 | 0.0 | 0.0 |
| 2-Methylnonane | – | 1.6 | 68.8 | 31.2 |
| 1-Bromo-3,7-dimethyloctane[a] | – | 1.6 | 56.3 | 43.7 |
| Pentane[b] | – | 5.0 | 50.0 | 50.0 |

Acid strength of the catalyst $SiO_2$–$H_2SO_4$: $H_O = -9.6$, temperature 295 K, reaction time 20 h, batch reactor (volume: 74 $cm^3$, catalyst amount: 0.1263 g, substrate: 0.2 $cm^3$, substrate (1:1 mixture with cyclohexane)/MCP ratio: 1:2)

2-MPr, 2-MB and MCP denote 2-methylpropane, 2-methylbutane and methylcyclopentane

[a] Catalyst acidity: $H_O = -10.6$

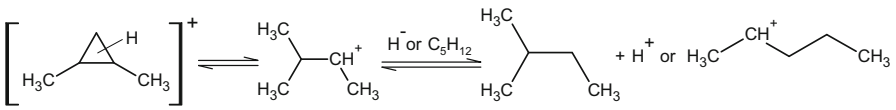
[b] Catalyst: $Al_2O_3-SO_4^{2-}$ (8 %)

## Discussion

Acid catalyzed reactions of light alkanes form the basis for one of the most important processes in the petrochemical industry i.e. alkane isomerization. For this reason, butane and pentane transformations initiated by acids have been the subject of numerous works. The mechanism operating in superacid solutions is generally accepted [23]. It begins (Scheme 1) with the protonation of the σ C–H bond in the pentane molecule (Scheme 1a) with the formation of a pentonium ion. The latter decomposes to hydrogen and a secondary pentyl cation (Scheme 1d). The carbocation isomerizes through a protonated cyclopropane transition state to another carbocation of a more branched carbon skeleton (Scheme 2).

The branched carbocation can undergo two hydride transfer reactions: with $H_2$ resulting in superacid molecule restoration as well as with another pentane molecule leading to the formation of a secondary pentyl cation. In the latter case, the catalyst is not recovered, thus the reaction becomes of a chain character. The mechanism of alkane isomerization is more complex for sulfated oxide catalysts. In such a case pentane, protonation is much less probable due to lower catalyst acid strength. It is then postulated that a pentyl cation is formed upon the abstraction of $H^-$ from pentane by strong Lewis acid centers [5, 15, 16]. Such active sites were found on the surface of the sulfated zirconia system [24]. Pentane to pentene dehydrogenation on redox centers is another possibility of the reaction initiation. Under the action of Brønsted acid sites of lower than superacid strength, the alkene forms a secondary pentyl cation. The latter reacts with the other pentene molecule to obtain a pentene dimer cation. Subsequent isomerization and β-scission leads to 2-methylpropane, 2-methylbutane and higher olefinic species—coke precursors (Scheme 1). The above discussion of pentane transformation mechanism indicates that irrespective on the way of the reaction is initiated all reaction pathways lead to the same transition state i.e. pentene and a secondary pentyl cation. A similar conclusion for butane transformation was presented by Hammache [25]. It is then interesting to follow the 1-pentene reaction, the main transition state precursor as a function of catalyst acid strength (Fig. 5).

1-Pentene begins to react if the acid strength of a catalyst reaches $-7$ $H_O$ units. One can observe the products of two reactions: isomerization (cis/trans 2-pentenes) and oligomerization (surface oligomer). With the rise of catalyst acid strength up to $H_O < -9$ 2-pentene isomers vanish, while pentene to surface oligomer conversion attains 100 %. A further increase in acid strength results in the oligomer decomposition with 2-methylpropane and 2-methylbutane appearance as new gaseous reaction products. At the same acid strength value, pentene dimeric cation precursors as 1-decene, 2-methylnonane and 1-bromo-3,7-dimethyloctane begin to




**Scheme 2** Isomerization of cyclopropane transition state for superacid catalyzed pentane isomerization

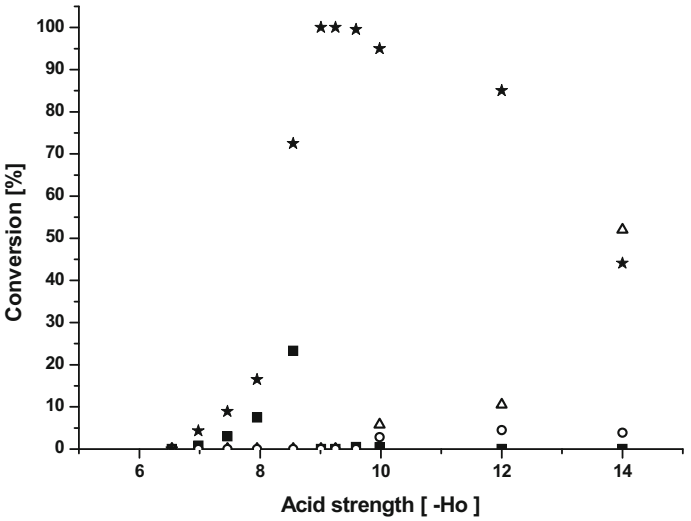



**Fig. 5** Dependence of 1-pentene conversion to: cis/trans 2-pentenes (*filled square*), pentene oligomers (*asterisk*), 2-methylpropane (*open triangle*) and 2-methylbutane (*open circle*) on catalyst acid strength [catalyst: $SiO_2$–$H_2SO_4$–$H_2O$, $SiO_2$–$F_3CCOOH$–$F_3CSO_3H$ or $SiO_2$–$FSO_3H$ 0.1263 g, temperature 295 K, reaction time 20 h, batch reactor (74 $cm^3$), substrate: 0.2 $cm^3$ (1:1 mixture with cyclohexane)]

react (Figs. 3 and 4). It is worth noting that in this acid strength region, n-pentane does not undergo any transformation.

The reactions with the different substrates have been performed over a catalyst of acid strength equal to −9.6 with or without the presence of hydride ion donor (methylcyclopentane) in order to study the possible transformation of both pentyl and decyl carbenium ions. The obtained results (Table 1) enabled us to notice the following regularities.

### 1-Pentene reaction

2-Methylpropane and 2-methylbutane formed in 2:1 ratio were the transformation products. This indicates a bimolecular pathway i.e. the reaction between pentene and pentyl cation followed by β-scission of the respective dimer cation (reactions h, i on Scheme 1). When methylcyclopentane was present in the reacting system, the obtained product ratio inverted to 1:2. It means that in the presence of $H^-$ ions, unimolecular isomerization of the secondary pentyl cation (Scheme 1e) and subsequent hydride ion transfer (Scheme 1f) mostly take place.

### 2-Bromopentane reaction

The change of secondary pentyl cation precursor from 1-pentene to 2-bromopentane does not substantially alter the reaction. The bimolecular transformation (Scheme 1g, h) and pentene dimer decomposition (Scheme 1i) leading to 2-methylpropane and 2-methylbutane (1:1 molar ratio) were observed. Unimolecular isomerization

(Scheme 1e) followed by $H^-$ transfer (Scheme 1f) takes place in the presence of methylcyclopentane. At the same time, 2-methylpropane to 2-methylbutane ratio becomes 1:8.

### 1-Pentene and 2-bromopentane reaction

If both pentene and bromopentane are present in the reacting system then probability of bimolecular reaction substantially increases. This is the reason for the high substrate conversion (Table 1). The ratio of 2-methylpropane to 2-methylbutane formed equal to 1:1 indicates that the reaction passes through a dimeric state (Scheme 1h) followed by the decomposition of decyl cation (Scheme 1i). In the presence of methylcyclopentane, secondary pentyl cations originated from both substrates undergo mostly unimolecular isomerization (Scheme 1e) and $H^-$ transfer (Scheme 1f), which results in the change of ratio of 2-methylpropane to 2-methylbutane ratio to the value of 1:4.

### 2-Bromo-2-methylbutane reaction

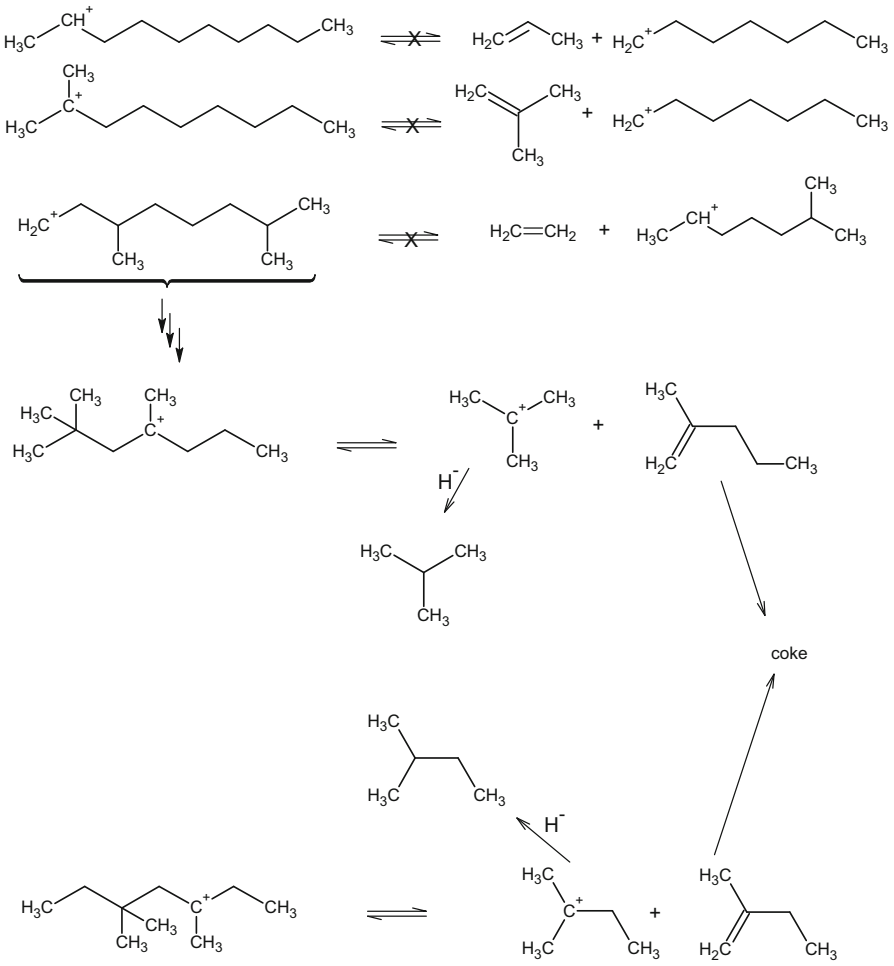
The tertiary pentyl cation, without or with $H^-$ reacts mostly with 2-methylbutane formation (Scheme 1f).

### 1-Decene, α-olefins $C_{12–24}$, 2-methylnonane and 1-bromo-3,7-dimethyloctane reactions

The first two compounds can be considered as secondary, linear, pentene dimer and oligomer cations precursors. They undergo β-scissions forming 2-methyl propane and 2-methylbutane in the 14:1 and 3:1 ratios, respectively. Such particular products can be produced if the secondary, linear carbenium ion undergoes chain isomerization (Scheme 3).

The reaction is slow [26], so the observed conversions are low (1.2 and 1.6 %, respectively). The branched carbocations with one (2-methylnonanyl) and two (3,7-dimethyloctanyl) methyl groups also react with low conversions because 2-methylpropane and 2-methylbutane would be obtained if further chain isomerization should proceed. Such a reaction can be accelerated when a catalyst with higher acid strength is used (Figs. 3 and 4). The results show that at $H_O = -14$, substrates such as 1-decene, 2-methylononane, 1-bromo-3,7-dimethylooctane and even decane react to 2-methylpropane and 2-methylbutane with conversions close to 100 %. In the presence of methylcyclopentane, the discussed reactions end. This means that under the reaction conditions, especially of low acid strength, decyl cations react faster with $H^-$ rather than undergo isomerization, which is crucial for decomposition.

It can be assumed that in the presence of a catalyst with acid strength $H_O \leq -9.6$, pentane does not undergo any reactions. Whereas, if a secondary pentyl cation appears in the reaction system it will undergo several transformations. The first one (bimolecular) consists of: isomerization, deprotonation, β-scission and $H^-$ transfer leading to two major products i.e. 2-methylpropane and 2-methylbutane formation. The other (unimolecular) includes: isomerization and $H^-$ transfer and




**Scheme 3** Possible pentene oligomer cations transformation during acid catalyzed pentane reactions

leads to 2-methylbutane. The choice of the pathway depends not only on a catalyst acid strength but also on $H^-$ accessibility in the system. If pentane alone is an only substrate, coke formation reactions can be considered a source of hydride ions and the transformation proceeds according to the bimolecular pathway.

Sulfated alumina containing 8 wt% of $H_2SO_4$ can catalyze pentane reactions at 295 K to 2-methylpropane and 2-methylbutane in 1:1 molar proportion (Table 2).

This indicates that the reaction proceeds according to the bimolecular mechanism through steps g, h and i (Scheme 1). In order to verify this, a reaction with 2-bromopentane as a substrate was performed. 2-Methylpropane and 2-methylbutane (molar ratio 1:2) were obtained as the products of the transformation just as in as in the case of the $H_O = -9.6$ catalyst. In the presence of $H^-$ ions, the ratio changes to 1:250. It indicates that the mechanism changed to the unimolecular pathway.

**Table 2** Pentane reaction. The transformation of carbenium ions precursors

| Substrate | $H^-$ donor | Conversion (%) | Selectivity (%) | |
|---|---|---|---|---|
| | | | 2-MPr | 2-MB |
| Pentane | – | 5.0 | 50.0 | 50.0 |
| 2-Bromopentane | – | 25.7 | 33.1 | 66.9 |
| 2-Bromopentane | MCP | 100.0 | 0.4 | 99.6 |
| 2-Methylnonane | – | 1.5 | 46.7 | 43.3 |
| 1-Bromodecane | – | 1.5 | 60.0 | 40.0 |
| 1-Bromodecane | MCP | 0.0 | 0.0 | 0.0 |
| Octane | – | 1.7 | 52.9 | 47.1 |
| 2,2,4-Trimethylpentane | – | 68.4 | 91.4 | 8.6 |
| 2,2,4-Trimethylpentane | MCP | 31.0 | 100.0 | 0.0 |

Acid strength of the catalyst $Al_2O_3/SO_4^{2-}$ (8 %), temperature 295 K, reaction time 20 h, batch reactor (volume: 74 $cm^3$, catalyst amount: 0.5 g, substrate: 0.2 $cm^3$, substrate (1:1 mixture with cyclohexane)/MCP ratio: 1:2)

2-MPr, 2-MB and MCP denote 2-methylpropane, 2-methylbutane and methylcyclopentane

Reactions of 2-methylnonane and 1-bromodecane were also performed to confirm the possibility of the involvement of decyl cations in the transformation. In both cases, 2-methylpropane and 2-methylbutane in a 1:1 molar ratio were identified as the reaction products. As in the case of $H_O = -9.6$ catalyst, the observed conversions were low and declined in the presence of methylcyclopentane. This further supports our earlier conclusion that chain isomerization of decyl carbenium ions is slow. It was more obvious when octane and 2,2,4-trimethyloctane (isooctane) were used as substrates. The conversion of linear-chain octane was low (1.7 %) while the branched octane isomer underwent the reaction with a much higher conversion (91.4 %). Moreover, the presence of $H^-$ did not influence the transformation of isooctane, whose structure prefers the β-scission of the respective carbenium ion.

The observed pentane transformation over $Al_2O_3{-}SO_4^{2-}$ (8 %) catalyst could indicate on superacid character ($H_O \leq -13$) of the surface. In our previous work [27], we carefully studied the acid strength of this catalyst by using the test reaction method. This method is based on the correlation of the test reaction results under the defined conditions (temperature: 303 K, batch reactor, catalyst: 0.5 g, substrate: 2 $cm^3$, reaction time: 20 h) with the minimal acid strength necessary to initiate the reaction ($H_{Omin}$ parameter). The results (Table 3) show that α-methylstyrene, styrene, 2,4-diphenyl-4-methyl-1-pentene, cyclohexene, 4-phenyl-1-butene and tert-butylbenzene undergo transformations, while cumene does not. This should indicate that the acid strength of this catalyst is equal to $-11.5 < H_O \leq -10.8$. This is certainly too low to catalyze pentane transformation by acid Brønsted centers. Therefore, the reaction has to be initiated by other active sites—most probably redox species. In our work [18], we showed that such centers are present on sulfated alumina surface. Thus, it is possible that the reaction proceeds according to pathway c (Scheme 1). The presence of pentene, the product of the oxidation of pentane, enables the occurrence of all transformation leading finally to 2-methylpropane and 2-methylbutane.

**Table 3** $Al_2O_3/SO_4^{2-}$(8 %). The results of acid strength measurements [27]

| Catalyst/conditions[1] | Test reaction results[2] (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| $H_O$ | −3.3 | −5.3 | −6.9 | −7.8 | −7.9 | −10.8 | −11.5 |
| | α-MS | St | dPh-4-M-1-P | CHXen | Ph-1-B | t-BB | Cum |
| $Al_2O_3/SO_4^{2-}$(8 %) | | | | | | | |
| a | | | | | | 1.3 | 0.0 |
| b | 100.0 | 100.0 | 100.0 | 66.1 | | | |
| c | | | | | 100.0 | | |

[1] Reaction conditions: 303 K, *a* catalyst 0.5 g, reactant 2 ml; *b* catalyst 0.5 g, reactant (30 % in heptane) 2 ml; *c* catalyst 0.5 g, reactant (10 % in heptane) 2 ml

[2] Conversion after 24 h into products of Brønsted acid catalyzed reactions; α-MS, St, 4-dP-2-M-1-Pe, CHXen, Ph-1-B, t-BB and Cum mean: α-methylstyrene, styrene, 2,4-diphenyl-4-methyl-1-pentene, cyclohexene, 4-phenyl-1-butene, tert-butylbenzene and cumene

## Conclusions

The transformation of n-pentane at 295 K begins most probably with the formation of a secondary carbenium ion. This is the result of the direct protonation of the C–H σ bond of a pentane followed by hydrogen evolution, which takes place in the presence of superacids of acid strength $H_O < -13$. In the presence of less acidic catalysts such as $Al_2O_3-SO_4^{2-}$ (8 %), pentane is oxidized to pentene, which is converted to the pentyl cation after protonation. The secondary pentyl cation is a key transition state in the reaction. It reacts in the presence of catalysts of acid strength of at least $H_O$ equal to −9.6 according to two pathways: (a) unimolecular in the excess of $H^-$ (in the presence of an additional, hydride donor pentane co-substrate) with the selective formation of 2-methylbutane; (b) bimolecular in the deficiency of $H^-$ (pentane alone is the substrate). In the latter case, the transformation proceeds through the formation of a ten-carbon dimer cation state, which upon decomposition leads to 2-methylpropane, 2-methylbutane and unsaturated coke precursors. For a given catalyst of acid strength $H_O < -9.6$, the n-pentane transformation pathway can be chosen by using a pentane co-substrate with hydride donating properties such as methylcyclopentane.

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